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54 **Clear gel detergent for automatic dishwashers.**

57 An optically clear aqueous gel detergent composition for automatic dishwashers is based on a high molecular weight polyacrylate resin matrix and water. The gel exhibits shelf-stability and detergency and has exceptional stability in the presence of a bleach ingredient such as sodium hypochlorite.

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## CLEAR GEL DETERGENT FOR AUTOMATIC DISHWASHERS

### Field of the Invention

The invention relates to detergent compositions and more particularly to detergent compositions useful for operating automatic dishwashers.

### Brief Description of the Prior Art

Automatic dishwashers are widely employed in homes and commercial food establishments. The prior art literature is replete with descriptions of detergent compositions, useful for operating automatic dishwashers. Representative of such compositions are those described in the U.S. Patents 4,431,559 (Ulrich, February 14, 1984); and 4,597,886 (Goedhart et al., July 1, 1986); British Patent 2,164,350 A (Lei et al., published March 19, 1986); and European Patent Application 0,239,379 (Brumbaugh, published September 30, 1987). The extensive patent literature relating to dishwashing compositions is an indication of the dissatisfaction in the art with available compositions. There has been a constant demand for improved compositions.

One improvement sought by the art has been the finding of compositions having improved stability, ie; long shelf-life. Also, marketing analysts have indicated a consumer preference for gel compositions, particularly optically clear gels.

The use of thixotropic mixtures composed of suspended clay, phosphates, alkali carbonates and other appropriate solids to provide opaque compositions as detergents (cleaning agents) for automatic dishwashers has also been known.

The compositions of the invention provide an optically clear gel, useful as a detergent for use in automatic dishwashing machines. The compositions exhibit exceptional stability, when stored for extended periods of time. The improvement is due in part to the use of a gel matrix which is a polyacrylate resin having a weight average molecular weight ( $M_w$ ) of more than 500,000, preferably at least 1,000,000 and most preferably within the range of from 3,000,000 to 4,500,000 Daltons (determined by gel permeation chromatography). Low molecular weight polyacrylates have been used in thixotropic dishwashing detergent compositions; see for example the European Patent Application 0,239,379 of Brumbaugh.

### Summary of the Invention

The invention comprises an optically clear aqueous gel detergent composition useful in automatic dishwashers to wash food preparation and serving utensils, which comprises:  
a composition base of a polyacrylate resin having a weight average molecular weight of more than 500,000 Daltons;

a water surface - tension reducing proportion of an anionic surfactant;  
a bleaching proportion of an oxidizing bleach; and  
sufficient of a detergent builder to complement the deterative action of the anionic surfactant; and  
a gel-forming proportion of water.

The compositions of the invention are true gels, dispersable in warm water and useful to wash food utensils in automatic dishwashing machines.

The term "gel" as used herein means a semi-solid system consisting of a network of solid aggregates in which a liquid is held.

A gel as defined herein is distinguishable from thixotropes, which are characterized by flowing under shear stress.

### Detailed Description Of The Preferred Embodiments of The Invention

The gel matrix or base for the compositions of the invention is a polyacrylate resin having a weight average molecular weight of more than 500,000 Daltons (determined by gel permeation chromatography and of sufficient  $M_w$  to form a gel with water. Preferably, the resin employed is the alkali metal salt, most preferably sodium polyacrylate. Sodium polyacrylate is a well known polymeric resin, as are methods of its preparation. The polyacrylates used herein include polymers and copolymers of acrylic acid, methacrylic acid and esters of these acids or acrylonitrile; see for example the Kirk-Othmer Encyclopedia of Chemical Technology, Second Edition, Vol. 1, pages 306-309.

The compositions of the invention include the polyacrylate resin in a proportion within the range of from about 0.5 to about 50 percent by weight, preferably 1 to 10 percent by weight.

The compositions of the invention also include a surface -tension reducing proportion of an anionic surfactant, to reduce the surface tension of the water with which the composition is mixed during dishwashing. Generally, a surface - tension reducing proportion is one within the range of from about 0.1 to about 10 percent by weight of the total composition. A wide variety of anionic surfactants are known as methods of their preparation.

Among the anionic surfactants useful in the present invention are those surface active compounds which contain an organic hydrophobic group containing from about 8 to 26 carbon atoms and preferably from about 10 to 18 carbon atoms in their molecular structure; and at least one water-solubilizing group selected from the group consisting of sulfonate, sulfate, carboxylate, phosphorate and phosphate so as to form a water-soluble surfactant.

Examples of anionic surfactants include soaps, such as, the water-soluble salts (e.g., the sodium, potassium, ammonium and alkanol-ammonium salts) of higher fatty acids or resin salts containing from about 8 to 20 carbon atoms. Other anionic surfactants are the alkane sulfonates including long chain alkane sulfonates and long chain hydroxyalkane sulfonates. Also the sulfated ethoxylated higher fatty alcohols of the formula  $RO(C_2H_4O)_mSO_3M$ , wherein R is a fatty alkyl of from 10 to 18 carbon atoms, m is from 2 to 6 (preferably having a value from about 1/5 to 1/2 the number of carbon atoms in R) and M is a solubilizing salt-forming cation, such as an alkali metal, ammonium, lower alkylamino or lower alkanolamino, or higher alkyl benzene sulfonate wherein the higher alkyls of 10 to 15 carbon atoms are present. The proportion of ethylene oxide in the polyethoxylated higher alkanol sulfate is preferably 2 to 5 moles of ethylene oxide groups per mole of anionic surfactant, with three moles being most preferred, especially when the higher alkanol is of 11 to 15 carbon atoms.

The preferred water-soluble anionic surfactant compounds are the ammonium and substituted ammonium (such as mono, di and tri-ethanolamine), alkali metal (such as, sodium and potassium) and alkaline earth metal (such as, calcium and magnesium) salts or the higher alkyl benzene sulfonates, and higher alkyl sulfates.

Most preferred as the anionic surfactant in the compositions of the invention are the water-dispersible, betains, amine oxides and the like which do not possess unsaturation in aliphatic moieties. Greatest preference is for the alkane aryls such as the Dowfax surfactants available from Dow Chemical Co., Midland, MI. These surfactants are alkylated diphenyl oxide disulfonates.

The compositions of the invention also contain a bleaching proportion of an oxidizing bleach such as for example, the chlorine bleaches previously employed in dishwashing detergent compositions. Representative of the chlorine bleaches are sodium dichloroisocyanurate and chlorinated trisodium hypochlorite. A bleaching proportion is generally within the range of from about 0.5 to 5 percent by weight of the total composition.

Also required as active ingredients of the compositions of the invention are sufficient of one or more detergent builders to complement the deterative action of the anionic surfactant. Detergent builders are known compounds that function, for example, by sequestering metallic ions present in water, reducing film formation in hard water caused by the precipitation of metals and providing alkaline cleaning power. The detergent builders include complex phosphates, carbonates, sulphates and silicates.

Representative water soluble phosphates include the polyphosphates, specific examples of which include sodium tripolyphosphate, potassium tripolyphosphate, tetrasodium monohydrogen tripolyphosphate, and trisodium dihydrogen tripolyphosphate. Especially preferred for use herein is potassium or sodium tripolyphosphate. Preferably, phosphates are present in the composition of the invention in a proportion of from about 0.5 to 5 percent by weight.

Representatives of water-soluble silicates for inclusion in compositions of the present invention include alkali metal silicates such as, for example, sodium and potassium silicates and metasilicates. Sodium silicates which have a  $SiO_2$  to  $Na_2O$  ratio of from 0.5:1 to 4:1 are preferred for use herein. Silicates may comprise from about 5% to about 40% by weight of the composition of the present invention.

Representative of carbonates preferably employed in the compositions of the invention are the alkali metal carbonates, most preferably potassium carbonate, employed in a proportion of from about 1 to 20 percent by weight of the total composition. The preferred potassium carbonate has an unexpected advantage in that it appears to stabilize the product gel against breakdown on prolonged storage.

Advantageously employed as an optional ingredient in the compositions of the invention are bleach stable volatile fragrances.

Volatile fragrances employed in the compositions of the invention include natural, essential oils and synthetic perfumes, and blends thereof.

The term "perfume" as used herein refers to odoriferous materials which are able to provide a pleasing fragrance and encompasses conventional materials commonly used in detergent compositions to counteract a malodor in such compositions and/or provide a pleasing fragrance thereto. The perfumes may be in the liquid state at ambient temperature. Included among the perfumes contemplated for use herein are materials such as aldehydes, ketones, esters and the like which are conventionally employed to impart a pleasing fragrance to liquid and gel detergent compositions. Naturally occurring plant and animal oils are also commonly used as components of perfumes. Accordingly, the perfumes useful for the present invention may have relatively simple compositions or may comprise complex mixtures of natural and synthetic chemical components, all of which are intended to provide a pleasant odor of fragrance when mixed in water. The perfumes used in detergent compositions are generally selected to meet normal requirements of odor, stability in bleach, price and commercial availability. A description of materials conventionally used in detergent perfumery is set forth by R.T. Steltenkamp, in The Journal of The American Oil Chemists Society, Vol 45, No. 6 pp.429-432, such disclosure being incorporated herein by reference thereto.

The fragrance is preferably substantially soluble in water and will not affect the optical clarity of the compositions of the invention. The fragrance may be added to the compositions of the invention in a fragrance emitting proportion. A fragrance emitting proportion is generally within the range of from 0.1 to 10 percent by weight of the total composition.

Many other optional additives such as foam control additives may be added to the compositions of the invention, as will be appreciated by those skilled in the art, provided that the addition does not adversely affect the stability or optical clarity of the compositions of the invention. The gel compositions of the invention must not contain fillers or carriers such as clay, which tend to result in unstable thixotropes, rather than stable gels.

The compositions of the invention are prepared by a homogeneous mixing of the desired ingredients in a gel-forming proportion of water. Each of the ingredients is admixed with the other ingredients in relative proportions to obtain the desired optical clarity, shelf-stability and dishwashing detergency. The admixture may be carried out in conventional mixing apparatus suited to the mixing of a gel composition.

A preferred method of preparing the compositions of the invention comprises stirring all of the ingredients together in water, except for the bleach and the fragrance. The resulting mixture is heated to a temperature of circa 50-100° C. with stirring to obtain a homogeneous mixture. The mixture is then allowed to cool to room temperature and the bleach and fragrance mixed in. The product is a gel.

In use, the polyacrylate-based aqueous gel compositions of the invention may be added to a dishwasher along with the food-soiled dishes. The dishwasher is then run through its wash and rinse cycles during which time it is dispersed in the wash liquor. The wash liquor is then repeatedly circulated through the spray nozzles whereupon it is brought in contact with soiled dish surfaces. The water temperature may vary but is usually in the range of 38° C to 60° C (100° F to 140° F). Under these conditions the gel disperses in the hot water. Typically, automatic dishwashers have two separate receptacles for dishwashing compositions to be added sequentially during the wash cycles. For example, a model manufactured by the Hobart Corporation, Kitchen-Aid Energy Saver V Superba, operates with two consecutive wash cycles. The first wash cycle lasts for three minutes, forty seconds and the second wash cycle last for four minutes, forty-five seconds. Each dishwashing composition receptacle holds approximately 30 grams. The first receptacle dispenses its contents at the beginning of the first wash cycle and the second receptacle dispenses its contents at the beginning of the second wash cycle. In use, the embodiment of the present invention which comprises a dishwasher detergent composition may be placed in the dishwashing composition receptacles inside a machine dishwasher in the manner previously described to be dispensed at the beginning of the first wash cycle and then at the beginning of the second wash cycle. Soiled dishes are, of course, placed inside the dishwasher and the washing process specified above is commenced. For most machine dishwashers, 30 to 60 grams of the detergent composition will adequately clean a full load of soiled dishes.

The following examples described the manner and process of making and using the invention and set forth the best mode contemplated by the inventors but are not to be construed as limiting. All parts are by weight unless otherwise indicated. Where indicated, the following test procedures were used.

#### Optical Clarity:

Light transmission was measured with a Spectronic 20-D instrument (Milton Roy Co.) and is reported as a percentage of the light transmission observed with a water standard (100 percent).

Viscosity:

Brookfield measurement with a No. 5 spindle at 10 RPM (reported in cps).

5 Stability:

An accelerated test method consists of heating a specimen in an oven at a temperature of 100° F. for a period of 4 weeks and then determining the loss of available chlorine and the loss of gel structure.

10 Example 1

The following ingredients were mixed together to obtain an optically clear aqueous gel:

<u>Ingredient</u>	<u>Weight (%)</u>
polyacrylic acid*	1.30
alkylated diphenyl oxide disulfonate**	2.00
sodium tripolyphosphate	15.00
20 potassium carbonate	7.00
sodium metasilicate	3.00
citrus fragrance	0.12
polydimethyl siloxane and silica***	0.10
25 sodium hypochlorite	8.34
sodium hydroxide	2.00
deionized water	<u>61.14</u>
	100.00

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\* Carbopol 940, B.F. Goodrich, Cleveland, Ohio, M<sub>w</sub>  
4,000,000 Daltons.

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\*\* Dowfax 2A1, Dow Chemical Co., Midland, MI.

\*\*\* Dow Corning Anti-foam A, Dow Chemical Co., Midland,  
MI.

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A mixture is prepared out by adding together the water, sodium tripolyphosphate, potassium carbonate, sodium metasilicate and sodium polyacrylate with stirring. The alkylated diphenyl oxide disulfonate is then feathered into the mixture and then heat is applied to bring the mixture to a temperature of 70° C., with continued stirring. With continued stirring, the mixture is allowed to cool to room temperature and then the  
45 remaining ingredients are mixed in and the mixture is then allowed to stand and gel. When tested, the gel product exhibited a light transmission of 76.4 percent, and a viscosity of 18,300 cps.

The gel product has a pH of 13.5 and demonstrates a superior stability compared to the presently marketed liquids which are thickened but opaque thixotrope products having a tendency to separate and settle on storage (15 percent loss of available chlorine and 10 percent loss of gel structure).

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Example 2

The procedure of Example 1, supra., is repeated except that in place of the sodium polyacrylate of M<sub>w</sub> 4,000,000 as used therein, an equal weight proportion of sodium polyacrylate M<sub>w</sub> 450,000 is used. The  
55 product is a liquid composition and not a gel.

Example 3

The procedure of Example 1, supra., is repeated except that in place of the sodium polyacrylate of  $M_w$  4,000,000 as used therein, an equal weight proportion of a sodium polyacrylate of  $M_w$  750,000 is used. The product is a thin gel.

#### 5 Example 4

The procedure of Example 1, supra., is repeated except that the proportion of water as used therein is reduced to 57.77 percent and the anhydrous sodium metasilicate as used therein is replaced with 6.37 percent by weight of sodium silicate (47.1 %). The product is a gel comparable to the gel of Example 1, supra.

#### Example 5

The procedure of Example 1, supra., is repeated except that the sodium tripolyphosphate as used therein is replaced with an equal proportion of tetrapotassium pyrophosphate to obtain a gel exhibiting a light transmission of 82.8 percent, a viscosity of 12,000 cps and a pH of 13.5. A shelf stability comparable to the gel product of Example 1, supra., was obtained.

#### Claims

- 20 1. An optically clear aqueous gel detergent composition which comprises:  
a composition base of a polyacrylate resin having a weight average molecular weight sufficient to form a gel with water;  
a water surface - tension reducing proportion of an anionic surfactant;  
25 a bleaching proportion of an oxidising bleach;  
sufficient of a detergent builder to complement the deterative action of the anionic surfactant; and  
a gel-forming proportion of water.
- 30 2. The composition of claim 1 wherein the oxidising bleach is sodium hypochlorite.
3. The composition of claim 1 or claim 2 wherein the detergent builder comprises a mixture of sodium tripolyphosphate, potassium carbonate and sodium metasilicate, preferably potassium carbonate.
- 35 4. The composition of any preceding claim which further comprises a fragrance emitting proportion of a fragrance ingredient.
- 40 5. The composition of any preceding claim wherein the weight average molecular weight of the polyacrylate resin is more than 500,000 Daltons, preferably within the range of 1,000,000 to 4,500,000 Daltons, more preferably within the range of 3,000,000 to 4,500,000 Daltons, especially about 4,000,000 Daltons.
6. The composition of any preceding claim wherein the anionic surfactant is selected from amine oxides, betains and alkylated aryl oxide sulfonates, preferably an alkylated diphenyl oxide disulfonate.
- 45 7. A composition according to any preceding claim in which the polyacrylate resin is present in the composition in an amount in the range 0.5 to 50% by weight, preferably 1 to 10% by weight.
8. A composition according to any preceding claim in which the surfactant is present in the composition in an amount in the range 0.1 to 10% by weight.
- 50 9. A composition according to any preceding claim in which the bleach is present in the composition in an amount in the range 0.5 to 5% by weight.
10. A composition according to any preceding claim which is an automatic dishwasher detergent composition.
- 55 11. A process for producing a gel according to any preceding claim in which the resin, surfactant, builder and water are mixed at a temperature in the range of 50 to 100 °C to form a homogeneous mixture, the

mixture is cooled to room temperature and the bleach and any fragrance are then mixed in.

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# EUROPEAN SEARCH REPORT

Application Number

EP 90 30 0914

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
X	EP-A-0 323 209 (UNILEVER) * Page 6, lines 30-34; examples; claims * ---	1-10	C 11 D 17/00 C 11 D 3/395
X	EP-A-0 346 112 (PROCTER & GAMBLE) * Page 11, line 60 - page 12, line 10; examples; claims * ---	1-10	
X	EP-A-0 314 061 (COLGATE-PALMOLIVE) * Page 4, line 56 - page 5, line 10; page 10, lines 1-24; examples; claims * ---	1-4, 6-10	
X	EP-A-0 264 975 (PROCTER & GAMBLE) * Whole document * -----	1, 2, 4-10	
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			C 11 D
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 24-09-1990	Examiner GOLLER P.
CATEGORY OF CITED DOCUMENTS			
<div>X : particularly relevant if taken alone</div> <div>Y : particularly relevant if combined with another document of the same category</div> <div>A : technological background</div> <div>O : non-written disclosure</div> <div>P : intermediate document</div> <div>T : theory or principle underlying the invention</div> <div>E : earlier patent document, but published on, or after the filing date</div> <div>D : document cited in the application</div> <div>L : document cited for other reasons</div> <div>&amp; : member of the same patent family, corresponding document</div>			